Phase Transfer-Catalyzed Preparation of Oxiranes

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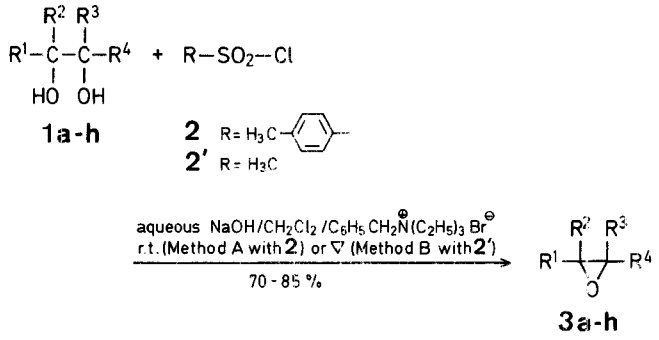
Oxiranes **3** are prepared in 70–85% yields by treating 1,2-diols **1** with one molar equivalent of *p*-toluenesulfonyl **(2)** or methanesulfonyl chloride **(2')** under phase transfer conditions.

The intramolecular nucleophilic displacement of a leaving group by an α-oxy anion represents a general method for the synthesis of oxiranes. Thus, halohydrins, as well as 1,2-diol

monosulfonates, sulfates, or nitrates react readily with alkali to afford epoxides in good yields[1]. Usually diols are transformed into oxiranes employing a two-step procedure via esterification to the monosulfonate and its subsequent treatment with base. We now report on a one-pot variant of this method which avoids the separation of intermediate esters.

Following our previously described preparation of sulfonic acid esters by treatment of alcohols with acid chlorides under phase transfer-catalyzed conditions (P.T.C. conditions)[2] we have now found that the reaction of 1,2-diols **1** with a molar equivalent of *p*-toluenesulfonyl (**2**) or methanesulfonyl chloride (**2'**) and aqueous sodium hydroxide solution in the presence of benzyltriethylammonium chloride results in a fast reaction giving the oxiranes **3**.



When *trans*-1,2-cycloalkanediols **1a–c** are treated with **2** under P.T.C. conditions at room temperature the sodium chloride and sodium sulfonate formed precipitate almost instantaneously. Examination of the reaction mixture by T.L.C. shows that the substrates were converted into the oxiranes **3a–e** after a few minutes. Sugar epoxides can be prepared in a similar way, for example methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-mannopyranoside **(3d)** from methyl 4,6-*O*-benzylidene-α-D-altropyranoside (**1d**; Table).

Enhanced yields of the corresponding oxiranes **3e–h** could be obtained by reacting acylic ethane diols **1e–h** with **2'** (Table). It is assumed that the intermediate sulfonates are formed primarily which then undergo intramolecular elimination. As is well established, the oxirane ring formation occurs only with an appropriate stereochemistry i.e. hydroxy group positioned to favour an S_N2 displacement leaving group[3]. In cyclic systems, the epoxides are formed from *trans*-diols **1a–d** whereas *cis*-1,2-cyclohexanediol cannot give oxirane **3b**. In conformationally mobile systems, the required antiperiplanar arrangement is readily achieved, leading to epoxide formation with inversion at the carbon atom bearing the leaving group as evidenced in the preparation of *trans*-1,2-diphenyl oxide **(3g)** from *erythro*-1,2-diphenyl-1,2-ethanediol **(1g)**.

We consider this one-pot preparation of oxiranes **3** from diols **1** to be a useful method, which owing to its ease, simplicity and mildness of conditions should be of general interest.

Oxiranes 3; General Procedure:

Method A: The two-phase system consisting of a solution of *trans*-1,2-cycloalkanediol (**1**; 0.1 mol) and benzyltriethylammonium bromide (1 g) in dichloromethane (200 ml) and 50% aqueous sodium hydroxide (50 ml) is equilibriated by vigorous stirring for 15 min. A solution of *p*-toluenesulfonyl chloride (**2**; 19 g, 0.1 mol) in dichloromethane (100 ml) is then added under cooling and maintain-

Table. Conversion of 1,2-Diols **1a–h** to Oxiranes **3a–h**

Substrate 1	Product 3	Method/ Time	Yield [%]	m.p. [°C] or b.p. [°C]/torr		n_D^{20}	
				found	reported	found	reported
1a	**3a**	A/10 min	71	100–102°/760	98–100/750[4]	1.4334	1.4341[4]
1b	**3b**	A/10 min	75	128–132°/760[c]	129–134°/760[5]	1.4512	–
1c	**3c**	A/10 min	82	86–89°/55	83–85°/50[6]	1.4618[c]	1.4615[c,6]
1d	**3d**	A/10 min	85	145–147°[c,d]	145–147°[7]	–	–
1e	**3e**	B/10 min	81	128–130°/20[c]	115–116°/4[8]	1.5312	1.53[c,8]
1f	**3f**	B/10 min	75	68–70°/20	69.7°/20[9]	1.4145	1.4150[c,9]
1g	**3g**	B/30 min	70	69–70°[d]	69–70°[10]	–	–
1h	**3h**	B/20 min	80	76–78°/12[c]	84–85°/12[11]	–	–

[a] Time required for complete consumption of starting diol [T.L.C.: benzene/ethyl acetate (2:1), detected with sodium metaperiodate benzidine reagent[12]].

[b] Yield of isolated product; 98% purity as determined by G.L.C. (column: 3 m × 4 mm, 5% SE30 on Chromosorb W-HMDS, 60–80 mesh).

[c] I.R. spectra in agreement with spectra of authentic sample.

[d] Crystallized from 70% ethyl alcohol.

[e] Refractive index measured at 25°C.

ing the temperature at 25°C. After stirring for another 10 min the mixture is poured into water (200 ml), the organic phase is separated, washed with water (3 × 50 ml), dried with sodium sulfate and distilled to give the pure product (Table).

Method B: A suspension of the acyclic ethanediol (**1**; 0.1 mol) and TEBA (1 g) in dichloromethane (100 ml) and 20% aqueous sodium hydroxide (100 ml) is stirred under reflux and a solution of methanesulfonyl chloride (**2'**; 11.5 g, 0.1 mol) in dichloromethane chloride (100 ml) added in portions. Heating and stirring is continued until complete consumption of the starting diol (T.L.C., eluent: benzene/ethyl acetate, 2/1), and subsequent work-up as in method A affords the product (Table).

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